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EXPERIMENTAL EVALUATION OF TANTALUM/STAINLESS STEEL MERCURY BOILERS FOR THE SNAP-8 SYSTEM

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TECHNICAL PAPER proposed for presentation at Fifth Inter-society Energy Conversion Engineering Conference sponsored by the American Institute of Aeronautics and Astronautics
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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Abstract

The greatest difficulties encountered in the utilization of mercury as the working fluid in a Rankine system have been the repeatability of the degree of fluid wetting of the heat transfer surfaces and the corrosion of the containment material by the working fluid.

A mercury boiler has been designed for the SNAP-8 system which utilizes tantalum for mercury containment. Four boilers of this design, designated as Serial No. 1, 2, 3, and 4, have been successfully tested over a wide range of operating conditions which encompasses the SNAP-8 system requirements. The Serial No. 1 unit was tested in a system loop at LeRC for 1444 hours and in a component test loop at the General Electric Company-Evendale for 13,661 hours. The Serial No. 2 unit was tested in the Power Conversion System Loop at Aerojet-General Corporation-Azusa for a period of 8700 hours and a total of 27 startups. Thus, the Serial No. 1 and 2 boilers have accumulated a combined total of over 23,000 hours at SNAP-8 system conditions. A third unit, Serial No. 3, which was utilized for system startup investigations at LeRC was subjected to 157 hours of operation and 135 startups and shutdown cycles. Based on the performance of the first three units, a new unit, the Serial No. 4, was built and tested in the PCS-1 test facility at AGC-Azusa.

The performance of the boilers and the post-test physical and metallurgical examinations of Serial Nos. 1 and 2 are discussed. The design modifications and performance of Serial No. 4 boiler are briefly reviewed.

Introduction

The SNAP-8 (Systems for Nuclear Auxiliary Power) program is developing a 35 kWe nuclear-electric power conversion system for space applications which utilizes a mercury Rankine-turbogenerator cycle. The system uses NaK-78 (eutectic sodium-potassium mixture) in the primary loop to transfer thermal energy from the reactor to the mercury boiler and in the heat rejection loop to convey waste energy from the condenser-subcooler to the radiator for rejection to space. The working fluid, mercury, is preheated, boiled, and superheated in the boiler; conveyed to the turbine-alternator assembly where energy conversion results in electrical power generation; condensed and subcooled and pumped back to the boiler to complete the cycle.

The greatest difficulty in the development of the SNAP-8 system has been the attainment of a reliable high performance boiler. The specific problem areas within the boiler were the wetting stability of the heat transfer surface and the corrosion resistance of the mercury containment material. These problems are not new in mercury boiler experience. Various authors (Refs. 1 to 3) have reported mercury wetting problems and the solubility of iron from low carbon and chromium-molybdenum steels in mercury at the high temperatures required in the mercury vapor stationary powerplants that have operated commercially since 1928.

Because of the limited strength of the low carbon and chromium-molybdenum steels, early mercury Rankine programs, SNAP-1 and 2, which operated in the same mercury pressure-temperature range as the stationary powerplants utilized austenitic stainless steels or the cobalt-based alloy, L605, as the mercury containment material. The choice of these materials was predicated on adequate strength at elevated temperatures; corrosion resistance to both NaK and mercury; compatibility with other materials in the primary NaK loop; stability at operating temperatures for a minimum of 10,000 hours; and light weight.

The SNAP-8 program, because of limited material choices, used L-605 in early boilers. However, prolonged exposure to the thermal environment of the SNAP-8 boiler, caused age hardening of the L-605 material (Ref. 4). This adverse characteristic and the increased rate of corrosion which resulted from the higher boiling temperatures of SNAP-8 system dictated an early search for an alternate material. This resulted in the selection of a refractory metal, specifically pure tantalum, as the mercury containment material.

Two boiler design concepts for incorporation of tantalum were initially considered. The first utilized a bimetal tube wherein a tantalum metal liner is metallurgically bonded in an austenic stainless steel tube. Several methods of tube fabrication were available which included hot coextrusion, explosive bonding, diffusion bonding, and vapor deposition processes. Each of these processes could have required extensive development. In addition, the attainable bimetallic tube lengths were insufficient to avoid complex tube/tube joints within the boiler shell. It was decided that this approach to the resolution of the boiler compatibility problem was difficult and would require significant development time and funding. The bimetallic tube development effort was therefore relegated to a backup status.

The second approach to the use of tantalum for the mercury-wetted portions of the boiler utilized a bare tantalum tube in a double containment concept. Three boilers of this design were built and tested. The design configuration for this concept (Fig. 1), thermal analyses, fabrication, and testing of the Serial No. 1 boiler at LeRC have been previously reported in Ref. 5. The results of the endurance testing and the post-test physical and metallurgical examination of Serial Nos. 1 and 2 are discussed herein. Serial No. 3 boiler which was utilized in the W-1 test facility at LeRC to investigate system transients is still in situ and is not discussed in this report. A fourth boiler, Serial No. 4, which incorporated major design changes, was built. A brief discussion of these changes and the performance of this boiler is presented.

Tantalum-Mercury Wetting Experiments

A series of wetting experiments and supporting analyses were conducted at Geoscience, Limited, Solana Beach, California (Ref. 6) to investigate the changes in thermal performance of a mercury-tantalum system. The principal results of these experiments were:

1. Chemically clean tantalum is wetted by mercury at temperatures in excess of 900° F.

2. In an oxygen-free environment, the tantalum will remain wetted for prolonged periods of time.

3. Oil or oxygen contamination will seriously affect heat transfer rates in mercury by orders of magnitude due to dewetting.

4. Oxygen contamination of the interior tantalum tube surfaces at elevated temperature, if not catastrophic, is a reversible process. Upon exposure to oxygen at elevated temperatures, the thin-walled tantalum tube surface will saturate in a short period of time and because of the high diffusion rate of oxygen in the tantalum and the presence of NaK on the tube exterior which acts as a sink for the oxygen, the oxygen can be absorbed by the NaK. This, of course, assumes that limited or no additional oxygen is supplied to contaminate the interior tantalum surfaces.

5. Oil contamination of the heat transfer surfaces results in a tightly adherent carbonaceous film. The presence of this film contributes two significant changes to the transfer of heat from these surfaces. The first, a change in surface chemistry, can cause a non-wetted condition between the mercury and the tube surface. A second mechanism is the increased thermal resistance which is added to the thermal path as a result of the presence of the surface deposit. The only available means of removing this film during boiler operation is by attrition of the film by the flowing mercury. The boiler performance during this period of operation can be seriously degraded. Fortunately, significant advances in loop operational techniques have minimized this problem. Recent operation of

the Serial No. 4 boiler in a system loop has indicated no degeneration of performance as a result of either extended operation or startup/shutdown cycling.

Mercury Boiling Design Considerations

The thermal and hydraulic performance predictions for the SNAP-8 boiler are based on single tube and full-scale development test results and analytical correlations. Since the boiler is a once-through vaporizer consisting of preheat, boiling, and superheat sections, the heat transfer mechanisms differ considerably. The SNAP-8 Ta boilers contain a multipassage plug insert in each of the seven mercury tube inlets. Each plug consists of sixteen parallel helical flow passages of small flow cross-sectional areas. The selection of this geometry is based on minimizing the formation of slug flow while limiting boiling pressure drop variations which result from boiler NaK inlet temperature excursions. Throughout the remaining tube length, a wire coil swirl insert is provided to impart centrifugal forces to the fluid, thus effecting a separation of the phases which accelerates the liquid droplets onto the heat transfer surface, the tube wall, and to tend to make the boiler's performance insensitive to the gravity environment.

A detailed evaluation of the boiler performance from a heat transfer viewpoint requires consideration of the local heat transfer coefficients as they vary along the boiler tube length through the various heat transfer regimes. The basic method of analysis is to subdivide the boiler length into a series of small increments and to write the coupling heat transfer and pressure drop correlations for each increment. The boiler preheat and superheat sections were subdivided by taking equal increments of the mercury temperature rise. Similarly, the wet vapor region was subdivided by taking equal increments of vapor quality. The solution of the coupling equations at each node provided the local thermal and dynamic operating parameters, increment length, and the node-boundary state conditions. Sequential solution of the nodal equations using standard computer techniques resulted in the analytical determination of the overall boiler performance (Ref. 5).

Thermal/Hydraulic Performance

From a system viewpoint, the boiler thermal and hydraulic performance aspects of most interest are the mercury exit thermodynamic state (the boiler is required to produce dry superheated vapor at all times) and the overall boiler pressure loss. Figure 2 shows the measured Serial No. 1 boiler inlet and outlet temperature conditions, as well as the measured NaK and estimated mercury local temperature profile variations both before and after the endurance test. It can be seen that the boiler produced essentially the same superheated mercury vapor exit conditions both before and after the endurance test. The local NaK-side temperature profiles are very similar, indicating small changes in local heat transfer performance. The main change in local performance over the endurance test period is an increase in the boiler tube length required to heat the inlet mercury to its boiling point (liquid heating region). This implies that the overall heat transfer coefficient in the plug region has decreased. Such a decrease could have been caused by a surface film buildup on either the NaK or mercury heat transfer surfaces. Post-test examination of the stainless steel tube which surrounds the tantalum tube in the plug region indicated the presence of an NaK oxide layer on its outer surface. The NaK oxide had been introduced into the boiler shell during prior loop operation at LeRC and was mechanically removed from the plug section prior to the endurance test. It is presumed that the remaining NaK oxide within the shell was redistributed along the tube and was the major influence in altering the thermal resistance in the plug section.

The boiler pressure loss measured before and after the endurance test, normalized to the boiler design point conditions, indicates that the boiler pressure loss decreased about 10 percent over the test period. This change is acceptable to the system. It is concluded, therefore, that the SNAP-8 boiler thermal/hydraulic performance is adequate and did not vary significantly with time over the endurance test period. The decrease in boiler pressure loss is quite consistent with the increase in liquid heating length as shown in Fig. 2.

The performance of Serial No. 2 boiler is illustrated in Fig. 3. The shellside NaK temperature profile as obtained from tests is shown compared to the analytical profile and indicates good agreement with the predicted performance. The analytical NaK shellside temperature profile, and the mercury temperature and pressure profiles were computed using the measured independent boiler parameters and an assumed 5 kWt external heat loss from the boiler. Extended operation of this assembly (8700 hr) and multiple restarts probably resulted in the introduction of oil contamination onto the heat transfer surfaces and the degradation of heat transfer in the plug region of the boiler. The overall boiler thermal performance, however, was not seriously affected as the boiler continued to produce dry superheated vapor throughout its operational life. As a result of these tests, it was concluded that the boiler performance met system requirements on overall performance and was predictable by the available analytical techniques.

Boiler Nos. 1, 2, and 3 had considerable excess superheat length as shown in Figs. 2 and 3. A new unit, designated Serial No. 4, was designed to reduce this margin and included significant mechanical thermal and hydraulic improvments. Figure 4 illustrates the comparison between the test and analytical data for Serial No. 4. As can be seen from these curves, a 30 percent reduction in heat transfer area was attained without affecting the boiler performance. In fact, the overall performance of Serial No. 4 boiler is better because of the smaller pressure drop changes which were observed due to NaK inlet temperature variations.

Post-Test Evaluation

Examination of the Serial No. 1 boiler materials following 15,105 hours of testing has indicated the excellent compatibility of the selected materials with liquid metals at high temperatures. No major corrosion or degradation modes were observed in any of the boiler components, and all indications point to a design life capability of at least 40,000 hours. The techniques, employed to evaluate the boiler materials following testing, included: visual, dimensional, and dye penetrant inspections; chemical analysis; metallographic examination; microhardness measurements; X-ray diffraction; and X-ray fluorescence.

Following extended testing of the Serial No. 1 boiler, the residual liquid metal inventories were carefully vacuum distilled from the assembly to prevent any contamination or reactions from cleaning fluids. The boiler was sectioned as shown in Fig. 5. The stainless steel-tantalum tube pairs were exposed by splitting the boiler shell. Subsequently, the boiler tubes were split longitudinal and both the tantalum and stainless steel tubes were carefully inspected. Visual examination indicated some discoloration of the materials but no signs of degradation. The stainless steel-tantalum bimetallic joints, the coextruded joint at the boiler inlet and the brazed joint at the boiler outlet, appeared unaffected by the test exposure.

A comprehensive metallographic examination of the component parts was performed. Sufficient specimens were randomly selected from each component to characterize the microstructures, and the observations which will be discussed are typical of that component.

Examination of the tantalum at the boiler inlet, as shown in Fig. 6(a), indicated a minor amount of corrosion on the static NaK side of the tantalum dished head. The attack shown extends to a depth of 2 mils and is typical of oxygen associated alkali metal corrosion along crystallographic planes. The morphology of the corrosion suggests the possible cause as being a slight oxygen contamination of the tantalum surface. The tantalum dished head at the boiler outlet showed no signs of attack although it operated at a much higher temperature (approx. 1300° F as compared to 600° F at the boiler inlet). Since the tantalum dished head at the inlet was replaced during a field weld repair some contamination could have occurred at that time. Chemical analysis indicates the oxygen concentration of the tantalum at the boiler exit to be less than 10 ppm as compared to 40 ppm at the boiler inlet. The difference in oxygen concentration could also be explained by differences in the kinetics of oxygen dissolution in the alkali metal as influenced by the temperature difference.

The cracked surface of the tantalum orifice, shown in Fig. 6(b), does not appear to be corrosion, but rather a result of machining. The orifices of this boiler were drilled but not reamed to finish dimensions. Subsequent units were finish-reamed.

Evidence of grain boundary penetration of the tantalum tubing in the plug area, as shown in Fig. 7(a), was found not to be initiated by mercury corrosion. If corrosion was the cause, the tantalum plug would be expected to show similar evidence. Examination of specimens of unused tantalum tubing, shown in Fig. 7(b), indicated similar defects. The liquid metal exposure would tend to accentuate these grain boundary voids. The defects in the as-received tubing could have resulted from surface contamination during processing followed by severe acid pickling. Similar grain boundary voids have been observed in Cb-1Zr tubing processed similarly; however, this effect is not typical of standard quality refractory metal tubing.

At the exit of the plug area and for the remaining length of the boiler a gray film was observed on the ID surface (mercury side) of the tantalum tubing. This phase, shown in Fig. 8(a), was approximately 1/2 mil thick. It is interesting to note that the phase extends down into a lap defect in the tantalum tubing shown to a depth of almost 4 mils. X-ray diffraction analysis of this phase indicated it to be predominately isomorphous with tetragonal Ni_3Ta; however, X-ray fluorescence analysis indicated the presence of iron, chromium, titanium, and some mercury in the coating as well as nickel. The mass transfer of stainless steel constituents occurs by dissolution of the stainless steel facility piping by the mercury and subsequent concentration in the boiler vapor region by evaporation of the liquid. The same phase was found on the tantalum turbulator wire which extended the full length of the open tube section of the boiler and the tantalum header and dished head at the boiler exit. Microhardness measurements indicated the phase to have Knoop hardness number of 361 as compared to an average hardness of 100 in the tantalum. Hardness decreases at the NaK side of the tantalum down to 70 Knoop indicated some oxygen depletion of the tantalum by dissolution in the static NaK.

No corrosion was observed in the stainless steel tubing. The areas adjacent to the surface were depleted in sigma as shown in Fig. 8(b) throughout the entire boiler. This effect was more prevalent on the flowing NaK side and suggests dissolution of some constituents in the stainless steel. Microprobe analysis, which is to be performed, should clarify this observation.

Comparative results of a limited examination of the Serial No. 2 boiler are shown in Figs. 6 and 9. In Fig. 6(a'), the tantalum dished head which was also replaced on this unit in the process of eliminating the bellows from the mercury circuit, indicated alkali metal corrosion. The degree of oxide contamination appeared to be greater than that experienced in the Serial No. 1 assembly. The corrosion penetrated to a depth of approximately 8 mils. The dished head on the boiler outlet indicated no appreciable signs of attack. The tantalum orifice of Serial No. 2 boiler (Fig. 6(b')) illustrates the beneficial effect of reaming. There are no signs of metal tearing or of corrosion of the tantalum. Figure 6(c) is a multiple fusion weld of the header/tantalum/orifice block which was employed as a seal weld in the boiler inlet. The exterior of this joint was exposed to liquid mercury and the outer and inner annular spaces between component parts were exposed to NaK and mercury, respectively. There are no signs of corrosive attack from either fluid.

Figure 9(a) shows the plug section of one tube of Serial No. 2 boiler after disassembly. Figure 9(b) is from a section of tube upstream of the fluted plug section. Figure 9(c) is a transverse section of the tantalum plug and tube. There are no signs of mercury corrosion in any of the material inspected to date.

Serial No. 4 Boiler

Based on the operational performance of Serial Nos. 1, 2, and 3 boilers a number of significant changes were incorporated into the design of the Serial No. 4 boiler (Fig. 10). This unit retained the same basic tantalum tube configuration as the prior units with the exceptions that the tube lengths were decreased to 25 feet and that the tubes were fully coiled. In addition, structural changes were included on the shellside of the boiler to attain a more uniform NaK flow distribution.

The boiler performance was previously illustrated in Fig. 4. In additon to the thermal performance improvements shown, the boiler mercury outlet pressure variations were less than ±1 psi as compared to ±5 psi variations on the prior tantalum boilers. The lower outlet pressure variation indicates an extremely stable boiler.

Conclusions

The successful operation of four double-containment, Ta-SS SNAP-8 boilers and the post-test inspection of two of these units which had operated for a total of 23,800 hours in either system and/or component test loops has verified the following:

1. Fabricability: The design and fabrication techniques employed on the four boilers have been proven by testing.

2. Mercury Containment: No detectable mercury corrosion or erosion of the tantalum has been noted on the boilers examined, Serial Nos. 1 and 2, which were tested for more than 23,000 hours.

3. Thermal Performance: Variations in boiler performance due to dewetting of the heat transfer surfaces has been reduced to acceptable limits for system operation by virtue of the following:

(a) Improved wetting characteristics of the tantalum

(b) High oxygen diffusion rates in the tantalum permits the recovery of the boiler thermal performance after exposure to limited oxygen contamination.

(c) Improved loop outgassing and operational techniques have, for all practical purposes, eliminated system contamination.

The results of the testing and analyses, which are described herein, indicates that all major problem areas which have impeded the development of a successful mercury boiler have been resolved. A long-lived, extremely stable, and reliable boiler, is available to meet the requirements of the SNAP-8 systems.

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E-5769

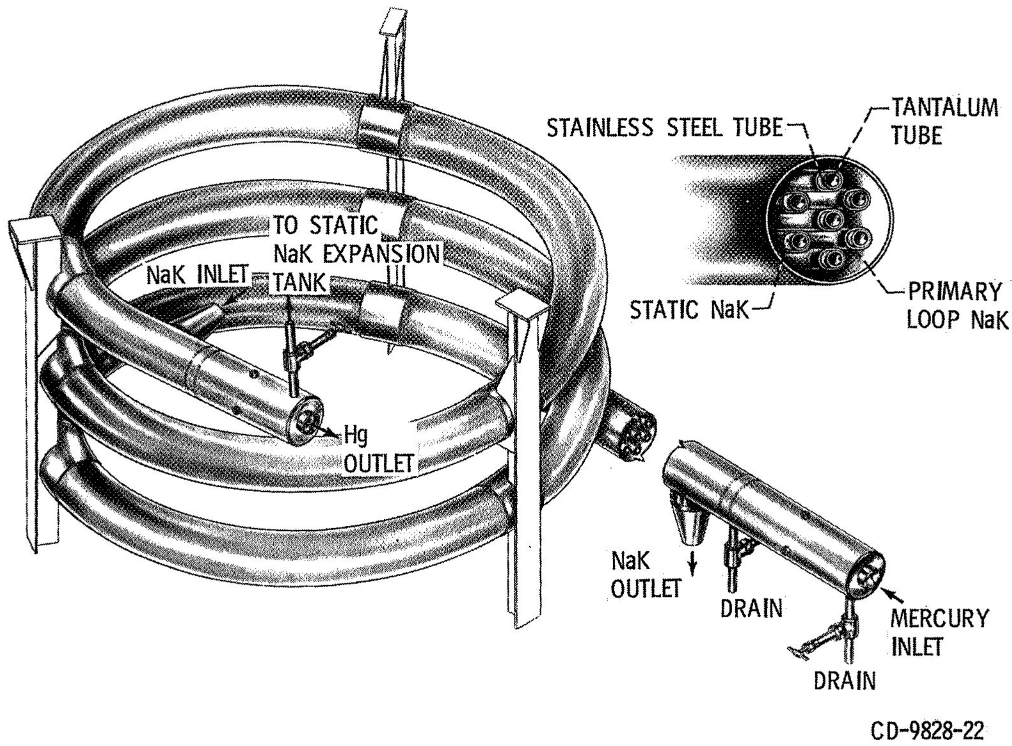

Figure 1(a). - SNAP-8 double containment Ta-SS boiler. Serial nos. 1, 2, and 3.

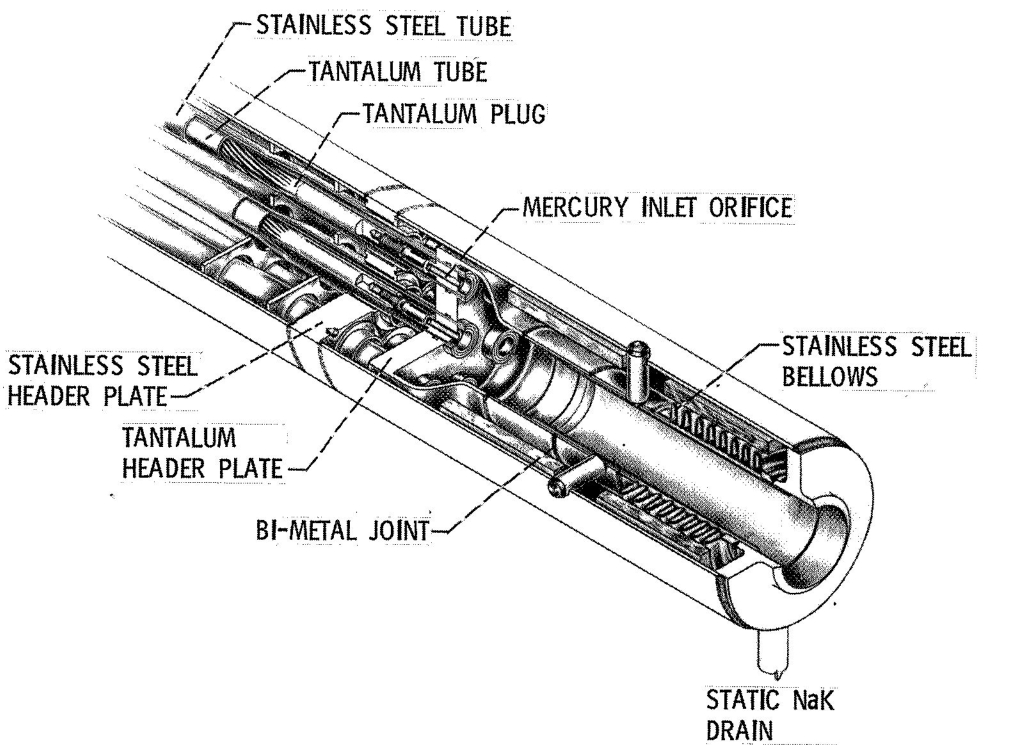

Figure 1(b). - Mercury inlet section.

E-5769

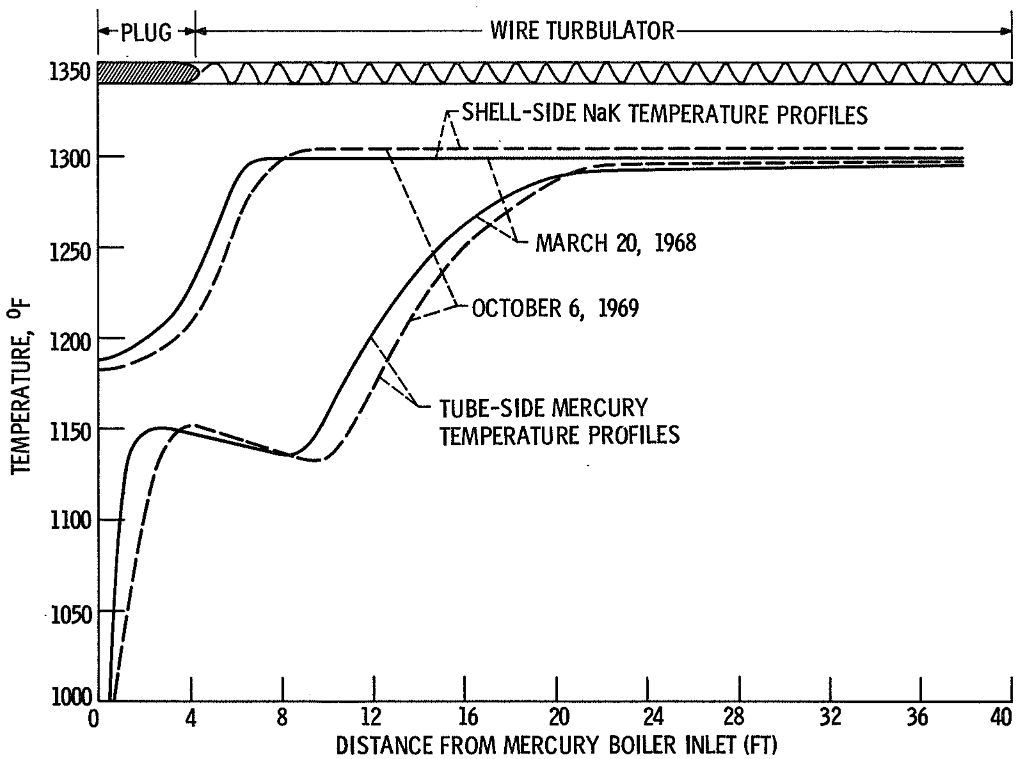

Figure 2. - Comparison of S.N. 1 refractory boiler temperature profiles taken before and after 10 000 hours endurance test at nominal system operating conditions.

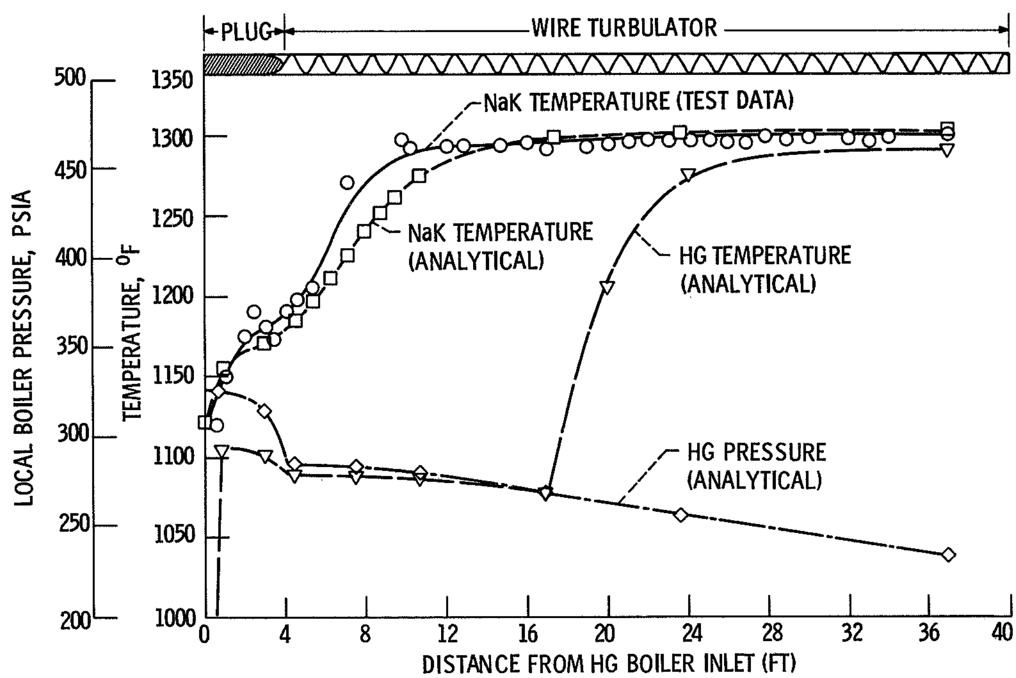

Figure 3. - S.N. 2 refractory boiler test data and analytical curves at nominal system operating conditions.

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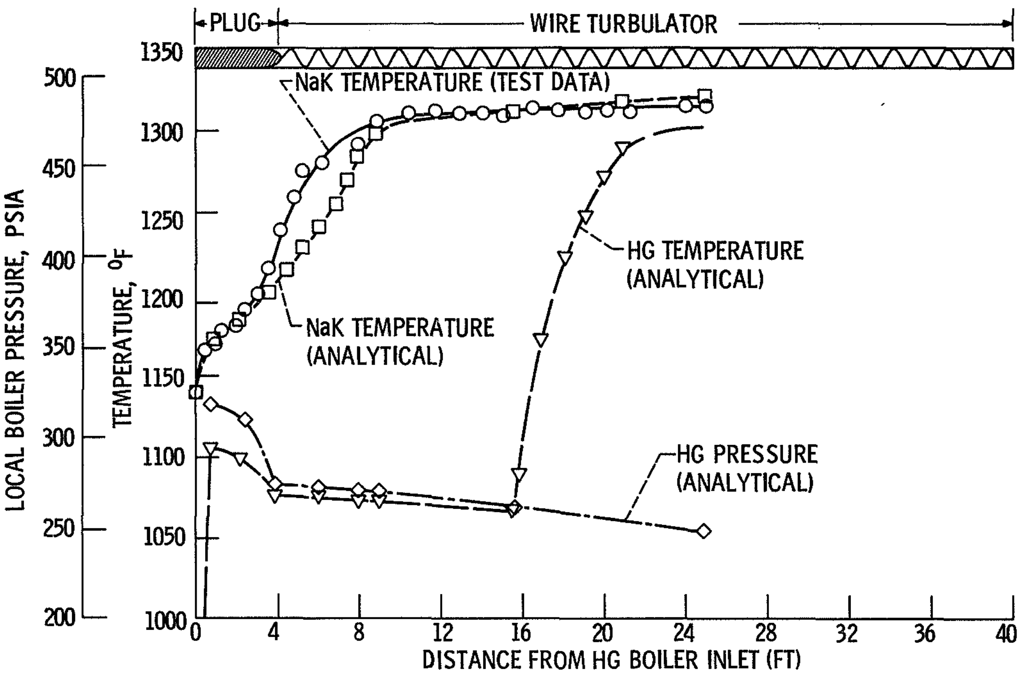

Figure 4. - S.N. 4 refractory boiler test data and analytical curves at nominal system operating conditions.

E-5769

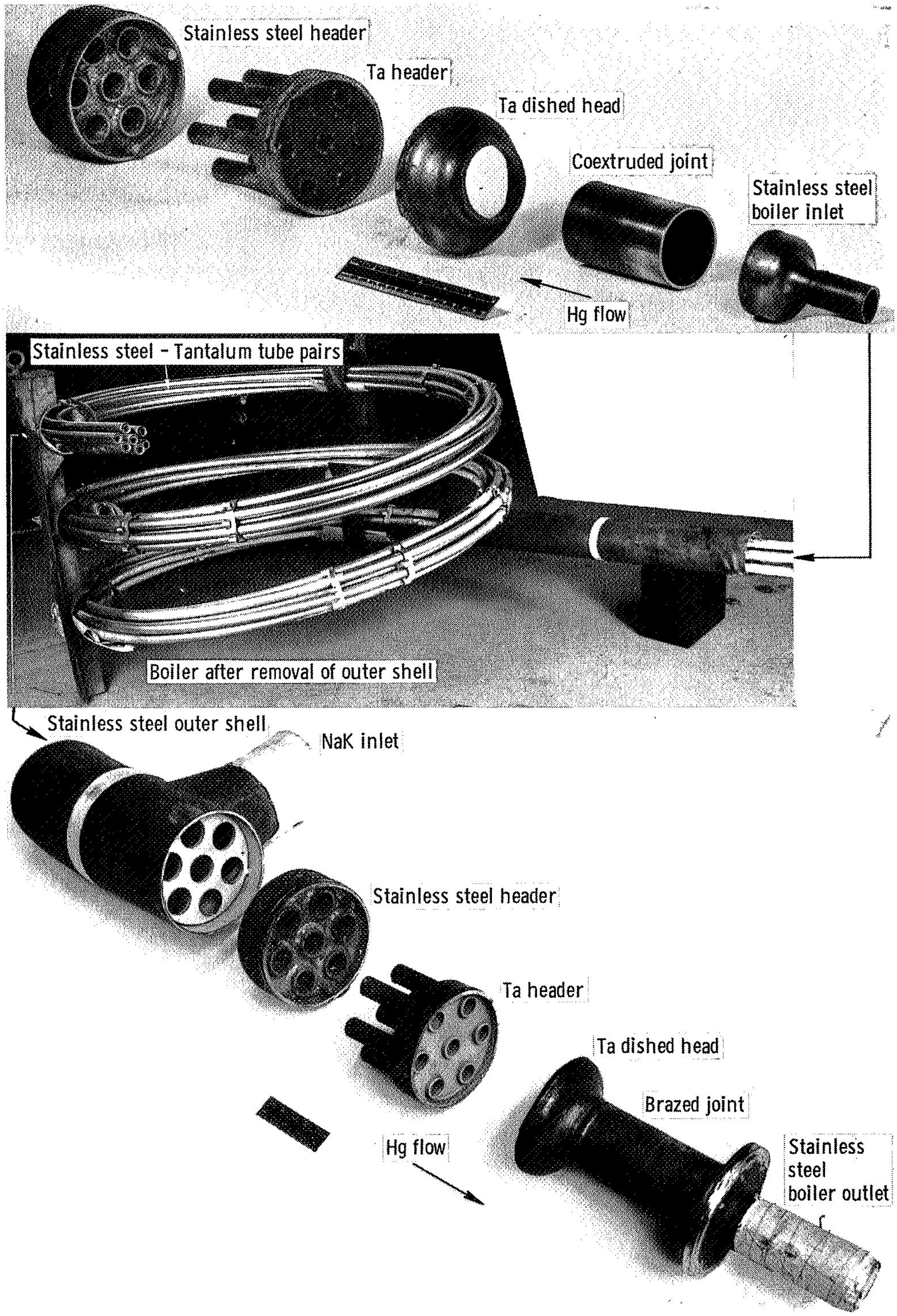

Figure 5. - Sectioned SNAP-8 S.N. 1 boiler after 15 105 hours of testing.

E-5769

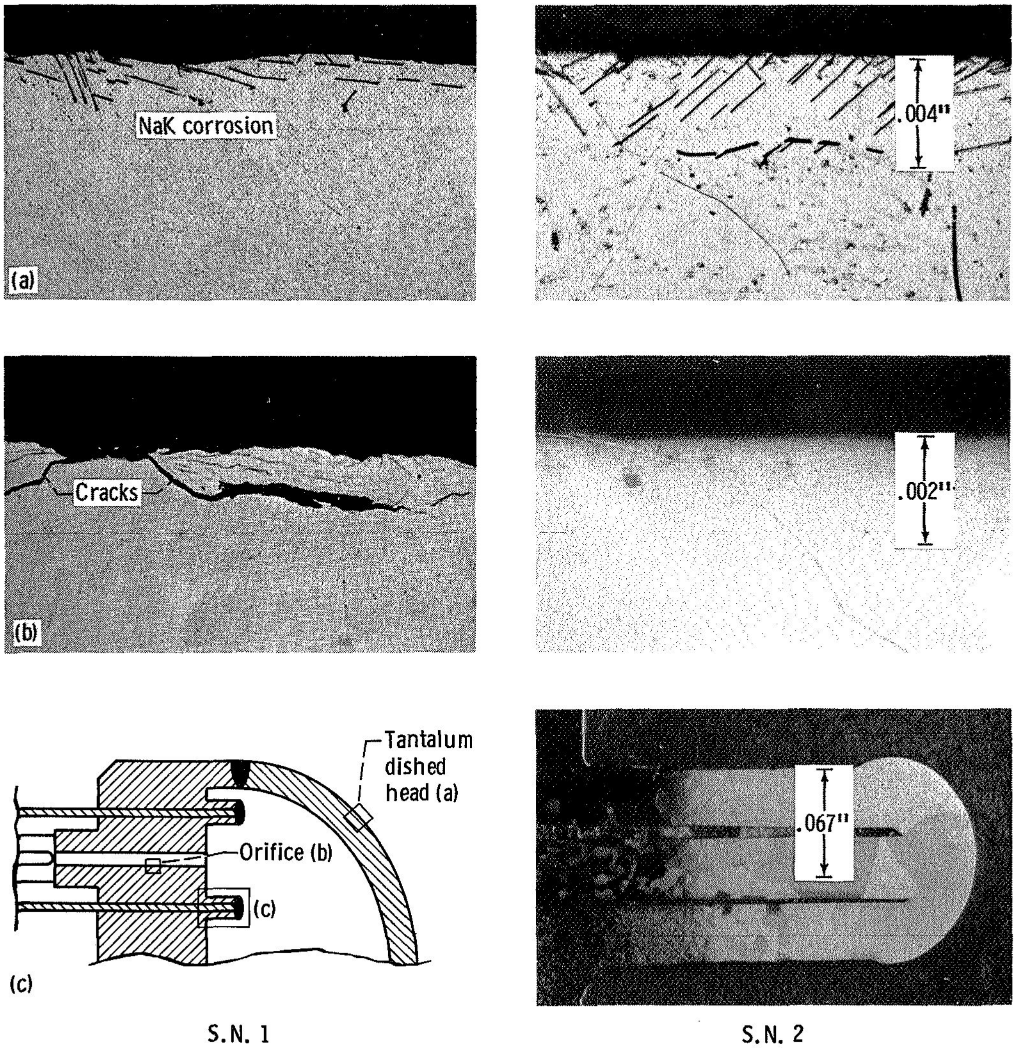

Figure 6. - Posttest microstructures of tantalum at boiler inlet. (a) NaK corrosion on the static side of tantalum dished head; (b) orifice (transverse section); (c) fusion weld-header, tube, orifice block. Comparisons of S.N. 1 and 2 boilers are shown.

E-5769

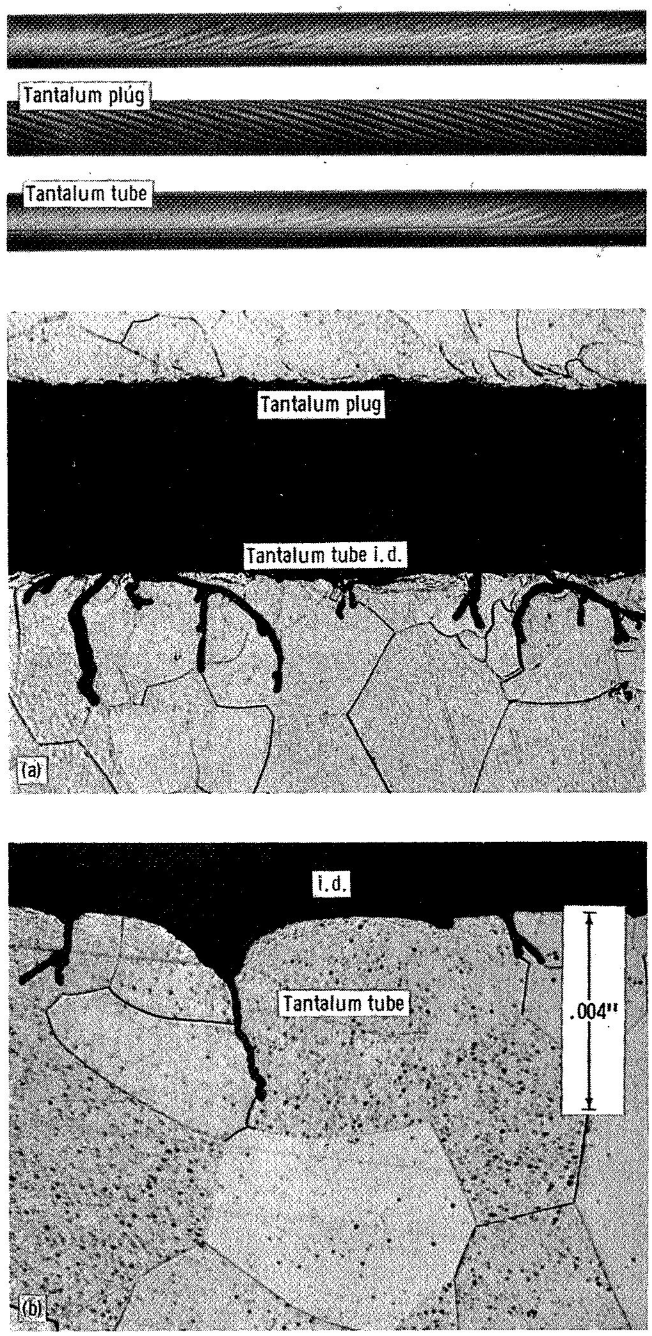

Figure 7. - Posttest microstructures of tantalum tube and plug from S.N. 1 boiler. The grain boundary voids observed in posttest tantalum tube (a) were similar to defects observed in untested tubing (b).

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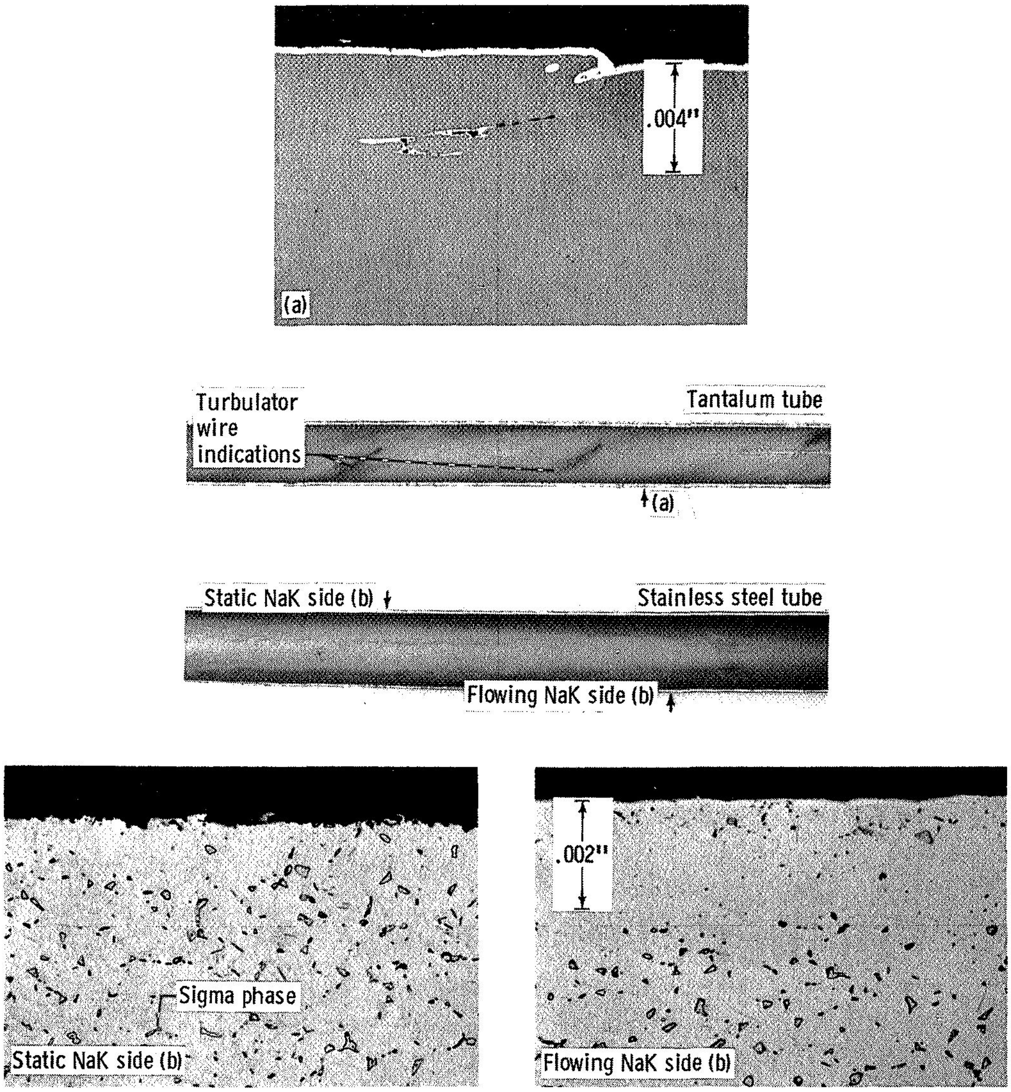

Figure 8. - Posttest microstructures of the stainless steel-tantalum tube pairs. The surface coating on the mercury side of the tantalum tubing (a) is isomorphous with Ni_3Ta. The surface of the stainless steel tubing exposed to flowing NaK shows more depletion of sigma phase than the surface exposed to static NaK.

E-5769

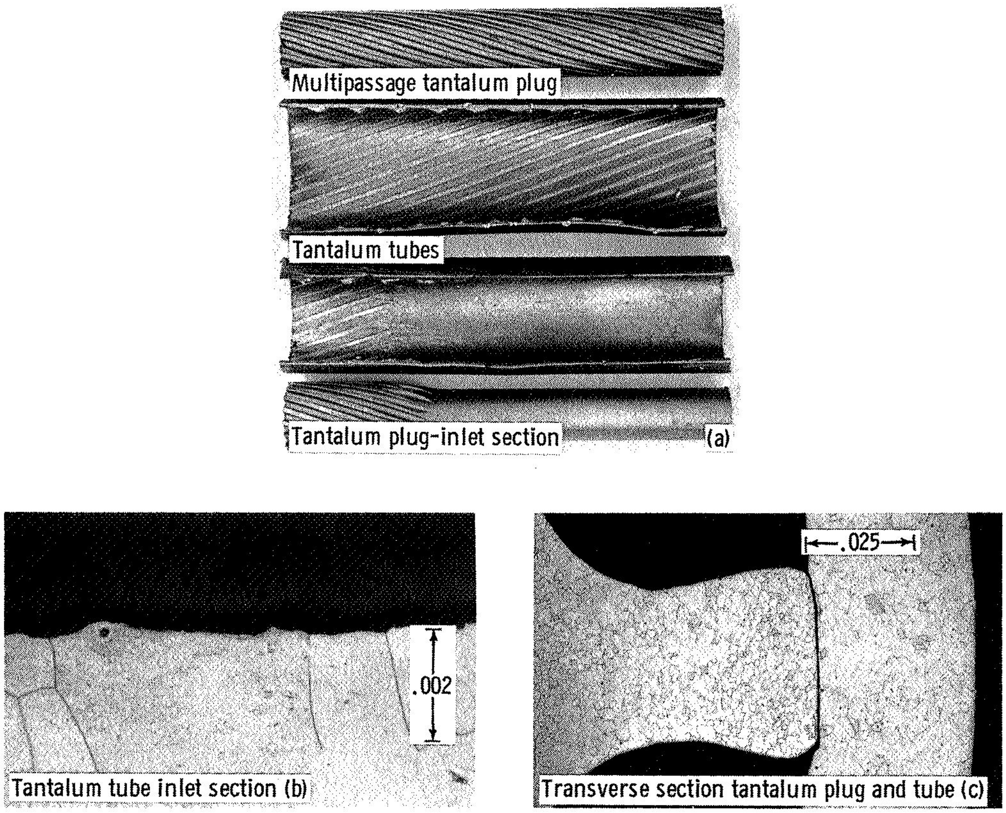

Figure 9. - Posttest microstructures of tantalum tube and plug from S.N. 2 boiler.

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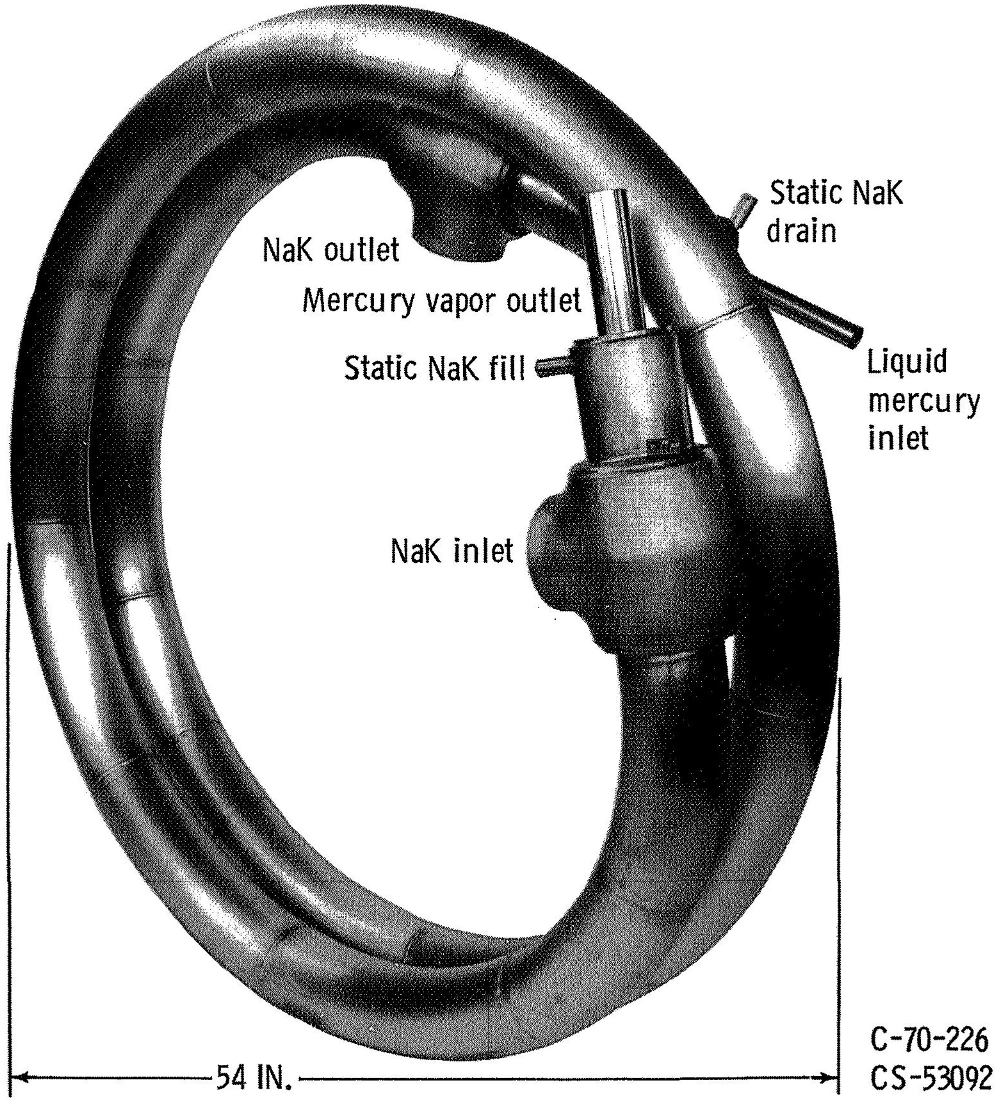

Figure 10. - SNAP-8 tantalum tube boiler, serial number 4.